PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements relating to the treatment of ferrous strip

We, THE PYRENE COMPANY LIMITED, a British Company, of Great West Road, Brentford, Middlesex, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Low carbon steel, silicon steel or other ferrous strip which emerges from a conventional hot-rolling mill usually has some residual rolling scale and corrosion products on its surface. The preparation of this strip for cold rolling normally involves passing it continuously through one or more pickling solutions and a rinsing solution and then through oil. Oiling is necessary because the strip can not pass directly to a cold-rolling mill as the speeds at which pickling and cold-rolling are carried out are different, and the strip has to be coiled before it is cold-rolled and may be corroded in the interval between pickling and cold-rolling. The application of oil is intended to prevent this, but suffers from several disadvantages. First, the oiling process is dirty and messy and the oil drips off the coils and second, on subsequent annealing of the strip the oil produces an undesirable smut.

If the oiling step is to be dispensed with it must be replaced by some other step which can be fitted into existing processes, that is to say the strip must be treated at the same speed at which it is pickled. Although actual speeds necessarily vary in different installations, this speed is usually between 150 feet/minute and 450 feet/minute. Now it has already been proposed to use phosphate coatings as an aid to the cold-deformation of various metals, but it has not hitherto proved possible to form phosphate coatings in the short time available in a continuous process of this type. For example, if the strip moves at 125 feet per minute a phosphate coating tank 25 feet long provides only about 10 seconds contact time. As the speed increases, either the phosphate coating tank must be greatly lengthened or the coating solution must act in a shorter time.

We have now found that certain phosphate solutions do form coatings in the short time available. According to this invention ferrous strip is prepared for cold-rolling by treatment with an aqueous, acidic zinc phosphate coating solution containing 0·05 to 1·5% by weight of zinc, 0·12 to 7·5% by weight of calcium, 0·4 to 2·5% by weight of phosphate, measured as PO_4, and an oxidising agent other than chlorate in an amount sufficient to produce a substantially uniform coating weighing at least 50 mg. per square foot in not more than 10 seconds. A substantially uniform coating is one which does not vary in coating weight at any point over the entire length of the strip by more than 200 mg./square foot from the average coating weight over the entire strip. The need for a substantially uniform coating arises in the subsequent cold-rolling; if the coating varies too much in weight the rolls of the mill tend to snatch and tear the strip especially where the coating is heavy. It is therefore preferred that the solution used can not form a coating weighing more than 1000 mg./square foot, most advantageously not more than 500 mg./square foot. Although the solutions used are preferably such that they will not form coatings weighing more than 1000 mg./square foot, provision may also be made for withdrawing the strip from the phosphate solution if the movement of the strip is interrupted. These interruptions arise from various causes, for example mechanical failures or to allow the ends of two strips to be joined or severed, and even with the preferred solutions if the strip remains stationary in the phosphate solution the coating formed on the immersed part of the strip, while still falling within the preferred limits, will be heavier than on the rest of the strip and this may lead to difficulty in cold-rolling. Various mechanical means for withdrawing the strip

may be used. For example, rollers at the inlet and outlet ends of the phosphate coating tank may be mounted on vertically movable elements which are actuated to raise the rollers at substantially the same time as the strip stops moving horizontally to remove the strip from the solution. Water sprays may be mounted above and below the strip to move into position after the strip has been raised and to spray the strip and rinse the phosphate solution from it. When the coating solution is being applied by spraying electrical interlocks may be provided which automatically shut off the sprays when the strip stops and start the water sprays from the same or different spray nozzles.

The cold rolling can be done on a reversing or multiple stand mill, employing the usual lubricants, such as mineral oil, palm oil and rape seed oil. These lubricants are preferably used in aqueous form, either as solutions or emulsions. Dilute aqueous solutions of 1% to 3% of a water-soluble mineral oil, or a lard-base oil together with an emulsifying agent for such oils may be used.

When the coating process of this invention is applied to continuously moving strip, the strip can pass continously through a pickling solution and then through the zinc phosphate solution. It is preferred that the strip is in contact with the solution for less than 20 seconds.

These coating solutions can be used under the usual conditions, for example, at strengths between 10 and 70 points and at temperatures from 100 to 195°F. The presence of calcium in the coating solution causes the production of somewhat finer grain coatings than if it were absent, and these coatings have been found to give the maximum assistance in the cold-rolling operation, i.e., in reducing the roll pressure required, the power required, and produce the smoothest, flattest strip having the best surface finish. For any particular actual concentration of calcium and zinc the ratio of calcium to zinc should be between 1:4 and 5:1 and preferably between 0·6:1 and 4:1.

Examples of suitable oxidising agents are nitrates, nitrites, sulphites, hypochlorites, periodates, hydrogen peroxide and organic nitro compounds such as picric acid, nitroguanidine, nitromethane, nitrourethane, nitraniline, nitrophenol, m-nitrobenzene sulphonate and dinitrobenzene sulphonate, bromates, iodates, t-butyl hydroperoxide and quinones. Nitrate and nitrite are the preferred oxidising agents. The solutions should contain 0·2 to 12% by weight of nitrate or other agent in equivalent amount. The ratio of oxidising agent to phosphate measured as PO_4 may be between 0·5 and 5·0 for nitrates, 0·001 and 0·05 for nitrites, 0·15 and 3·0 for m-nitrobenzene sulphonate, 0·002 and 0·01 for hydrogen peroxide and 0·1 and 1·5 for dinitrobenzene sulphonate. Mixtures of oxidising agents can also be used. Chlorate is unsuitable as an accelerator, since the coatings produced do not improve the behaviour of the strip during cold-rolling.

The phosphate coatings of this invention, after conventional cold water-rinsing, assist in the prevention of corrosion of the strip during the delay prior to rolling and completely eliminate the need for the conventional oiling step. In instances where the conditions which cause corrosion are worse than usual, it may, however, be desirable to rinse the coated surface with, for example, a dilute aqueous solution of chromic acid, borax, sodium nitrite or soda ash.

It is preferred to activate the strip after it has been pickled and before it is coated by treating it with an aqueous solution of oxalic acid; of disodium phosphate of tetra-sodium pyrophosphate containing titanium or zirconium; of tetra-sodium pyrophosphate; of a mixture of tetra-sodium pyrophosphate and a metaphosphate; of a dialkali metal phosphate containing up to 0·05% of lead, tin or arsenic; or of a mixture of tetrasodium pyrophosphate and disodium phosphate containing titanium or zirconium. This treatment activates the surface of the strip and makes it more receptive to attack by the phosphate solution. Moreover, by using this additional step it is found that coatings can be formed in 8 seconds, or in some cases even 3 seconds. Examples of suitable titanium compounds are titanium chloride, titanium hydroxide, titanium nitride and titanium potassium oxalate; up to 0·05% by weight of titanium should be present.

Examples of solutions which form substantially uniform coatings are those having the following analyses (percentages being w/v):

A. Zinc 0·19%, nitrate 0·30%, PO_4 1·38%, nitrite 0·006%, calcium 0·14%, free acid 1·5 and total acid 15·6.

B. Zinc 0. 35%, nitrate 1·55%, nitrite 0·006%, PO_4 0·84%, calcium 0·34%, total acid 20·2, and free acid 2·7.

C. Zinc 0·17%, nitrate 1·18%, PO_4 0·92%, iron 0·16%, calcium 0·28%, total acid 20·8, free acid 3·0.

D. Zinc 0·21%, nitrate 2·17%, PO_4 0·64%, calcium 0·53%, nitrite 0·004%, total acid 15·1, free acid 1·8.

Examples of suitable activating solutions are a solution of 2% by weight oxalic acid in water, which may be used at room temperature with a contact time of thirty seconds; a 1% solution of disodium phosphate in water containing between 0·005% and 0·05% of titanium as a soluble titanium compound, believed to be titanium chloride, which may be used at 190°F with a contact time of thirty seconds; and an aqueous solution, containing 0·87% w/v of tetrasodium phosphate,

0·13% w/v of disodium phosphate, and between 0·005% and 0·05% of titanium, which may be used with a contact time of one minute at 160°F.

WHAT WE CLAIM IS:—

1. A process which comprises the steps of forming a substantially uniform phosphate coating on a ferrous strip by treatment with an aqueous, acidic zinc phosphate coating solution containing 0·05 to 1·5% by weight of zinc, 0·12 to 7·5% by weight of calcium, 0·4 to 2·5% by weight of phosphate, measured as PO_4, and an oxidising agent other than chlorate in an amount sufficient to produce a substantially uniform coating weighing at least 50 mg./square foot in no more than 10 seconds, and cold rolling the phosphate-coated strip.

2. A process according to Claim 1 in which the strip passes continuously through a pickling solution and then through the zinc phosphate solution and is in contact with the latter solution for less than 20 seconds.

3. A process according to Claim 1 or Claim 2 in which the ratio of calcium to zinc is between 0·6:1 and 4·0:1.

4. A process according to any of the preceding claims in which the zinc phosphate solution contains 0·2 to 12% by weight of nitrate as the oxidising agent, or other agent in equivalent amount.

5. A process according to any of the preceding claims in which the strip, after being pickled and before being phosphate-coated, is activated by treatment with an aqueous solution of oxalic acid; of disodium phosphate or tetrasodium pyrophosphate containing titanium or zirconium; of tetrasodium pyrophosphate; of a mixture of tetrasodium pyrophosphate and a metaphosphate; of a dialkali metal phosphate containing up to 0·05% of lead tin or arsenic; or of a mixture of tetrasodium pyrophosphate and disodium phosphate containing titanium or zirconium.

6. A process according to any of the preceding claims in which the zinc phosphate solution is such that it cannot form a coating weighing more than 1,000 mg./square foot.

7. A process according to Claim 1 in which the phosphate-coating solution used is any of solutions, A, B, C and D.

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